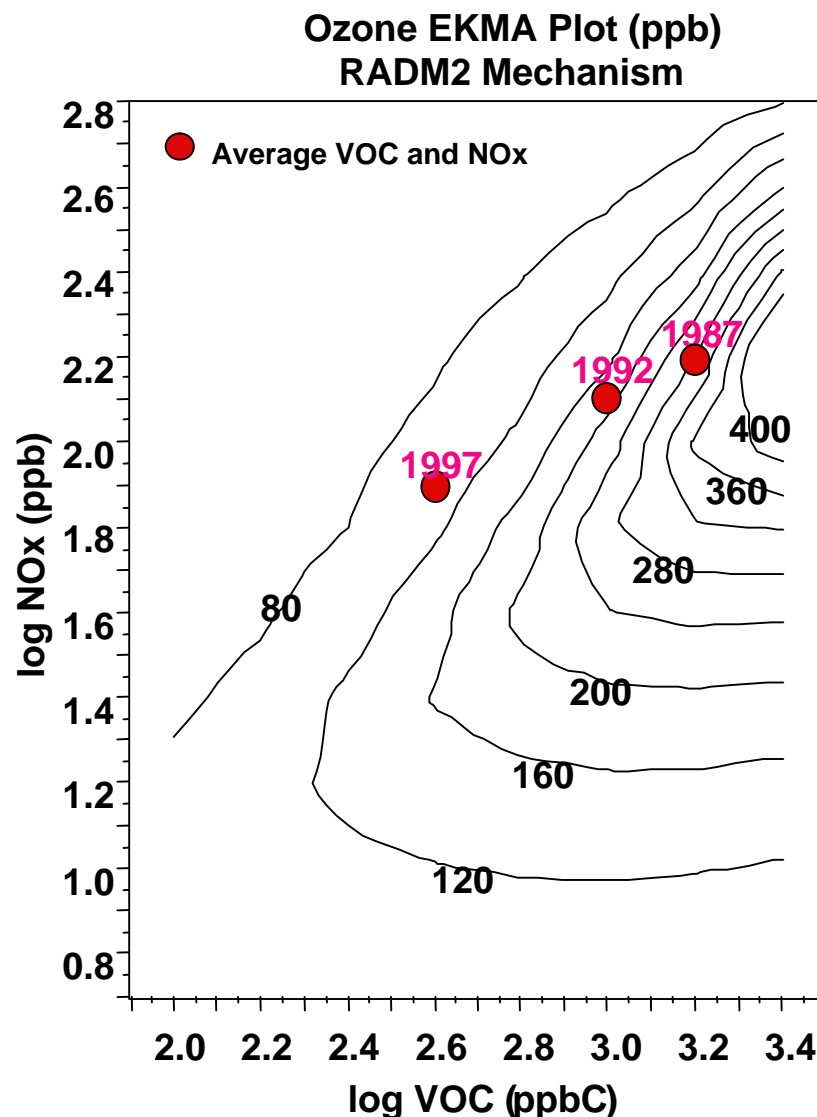


The Relationships Between NO_x , NO_y , and Ozone

- Introduction
- Monitoring Issues
- Analyses Using NO_x , NO_y , and Ozone Data
- VOC and NO_x Limitations
- Analyses Using VOC/ NO_x Ratios
- Relationships of Ozone, NO_y , and NO
- Indicator Methods
- Observational-Based Modeling, Smog Production Algorithms, and MAPPER
- Other Methods
- Analyses Along a Transport Path
- Method and Tool Availability
- Summary
- References

Introduction

- Emission control strategies are based on assessments of whether an area is "VOC-limited" or "NO_x-limited."
- No single analysis should form the basis for these decisions. Rather, several analyses, plus modeling, should provide concurrent evidence (i.e., consensus).
- This section explores analytical techniques which use NO_x, NO_y, ozone, and other species data to assess control strategies.

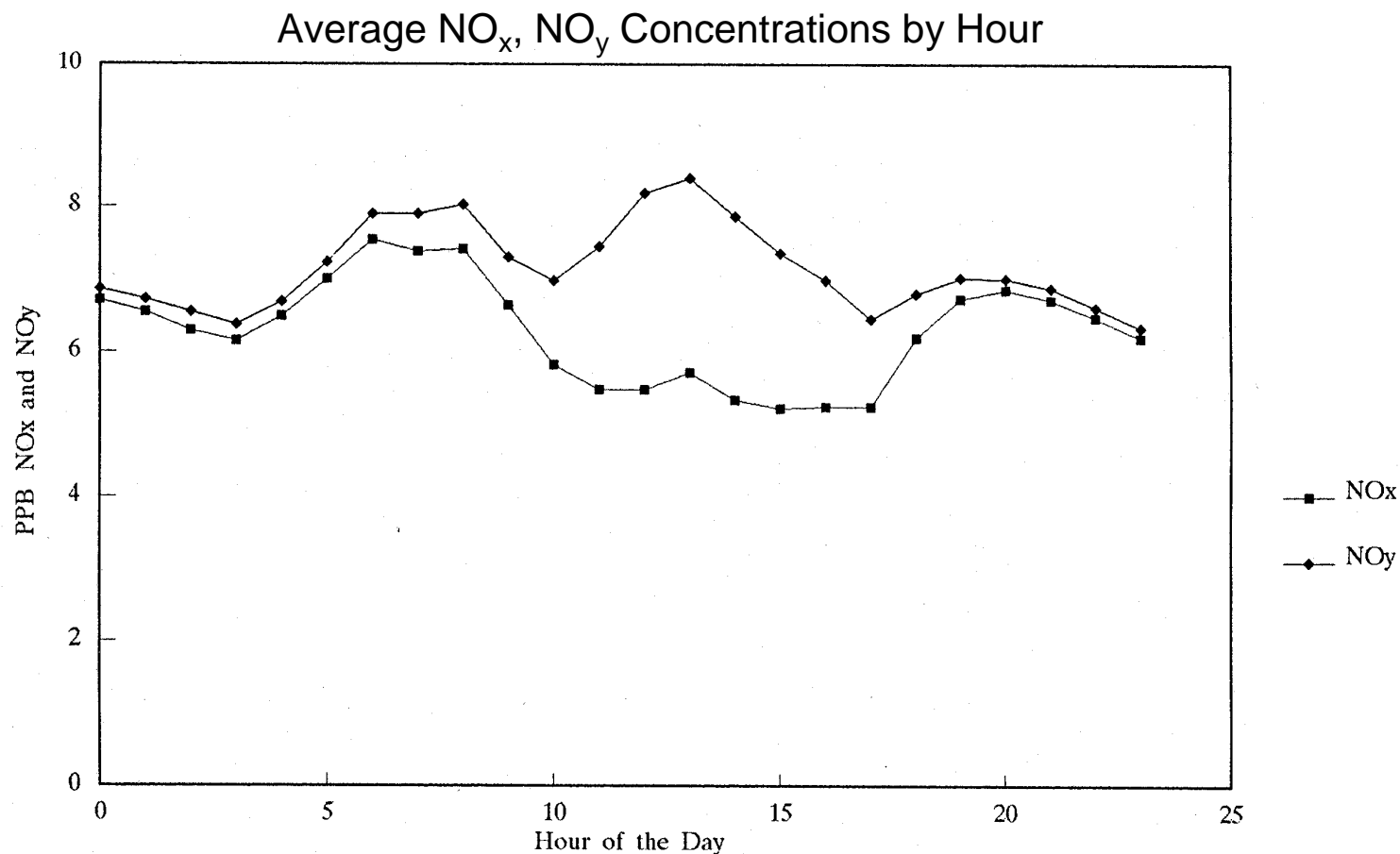


Fujita et al., 2000

Monitoring Issues

- Most NO_x instruments measure NO, NO_2 , and a poorly defined fraction of other nitrogen species. Thus, NO_x instruments can be biased high. This problem is exacerbated in rural locations where the NO_y/NO_x ratios are high relative to urban locations with fresh NO emissions.
- NO_y instruments attempt to quantify NO and the sum of NO_x , HNO_3 , organic nitrates, and inorganic nitrates.
- Current networks emphasize urban measurements of NO_x ; thus, urban to rural gradients are not well characterized.
- Siting issues for NO_x monitoring exist. For example, how does an analyst determine the influence of fresh, local NO_x emissions?
- Some agencies are replacing NO_x monitors with NO_y monitors. How does this affect trend analyses?

Comparing NO_x and NO_y Concentrations



The differences between NO_y and NO_x at a site may vary over the course of the day.

Diurnal average patterns of NO_y and NO_x from two measurement systems at a rural site in Pennsylvania in summer 1994 (Kelly et al., 1995). Under nighttime conditions, deposition of HNO₃ would occur rapidly, and that of other species more slowly. Thus, NO_y is depleted of species that are difficult to sample and NO_y and NO_x compare well. During the day, photochemical processes convert NO_x to product species which the NO_y monitor does a better job of measuring. Note that the relative (not necessarily the absolute) difference might be more pronounced at a rural site.

Analyses Using NO_x, NO_y, and Ozone Data

In this section of the workbook, the following analyses are discussed:

- VOC/NO_x ratios have been used widely as one method to assess whether NO_x and/or VOC controls would be effective to reduce ozone.
- The relationship between ozone, NO_y and NO_x, and other pollutants can also be useful in assessing NO_x versus VOC controls.
- Other “indicator” ratios have been assessed to help identify NO_x limitations. Some of these ratios require special studies data (i.e., non-PAMS measurements).
- Extent of reaction indicates whether ozone formation, at a specific place and time, is limited by the availability of VOCs or NO_x.

VOC and NO_x Limitations (1 of 2)

- The ratio of VOC to NO_x or NO_y in the morning is an important parameter for photochemical systems. The ratio characterizes the efficiency of ozone formation in VOC- NO_x-air mixtures.
- At low ratios (< 5 ppbC/ppb), ozone formation is slow and inefficient (i.e., VOC-limited or VOC-sensitive chemistry). Decreasing NO_x levels may result in increased ozone formation.
- At high ratios (> 15 to 20 ppbC/ppb), ozone formation is limited by the availability of NO_x rather than VOC (i.e., NO_x-limited or NO_x-sensitive chemistry).
- Ratios between 5 and 15 are considered transitional, and both NO_x and VOC controls may be effective.
- The ranges of ratios used to define VOC- and NO_x-limitations varies among researchers.

VOC and NO_x Limitations (2 of 2)

- Ratios may change during transport of air parcels; therefore, the analyst needs to consider the effects of controls on both nearby areas and areas far downwind.
- Typically, though not always, freshly emitted pollutants are characterized by VOC-sensitive chemistry and evolve towards NO_x-sensitive chemistry as the air mass ages.
- In general, NO_x emissions within an urban area determine the total amount of ozone that is formed after the air moves downwind and chemistry has run to completion, while VOC emissions control the rate of the initial buildup of ozone.

Reductions in VOC will only be effective in reducing ozone if VOC-sensitive chemistry predominates.

Reductions in NO_x will be effective only if NO_x-sensitive chemistry predominates and may actually increase ozone in VOC-sensitive regions.

Analyses Using VOC/NO_x Ratios (1 of 3)

The analyst needs to consider the following:

- What comprises VOC in VOC:NO_x?
 - Is methane included in the definition of VOC? *Traditionally, only non-methane hydrocarbons are included.*
 - Are biogenics (e.g., isoprene, terpenes) included in the VOC? *While some researchers have excluded the biogenics from analyses, most do include these hydrocarbons, when available.*
 - Are carbonyl compounds included? *Again, when available, these measurements have been included by some and excluded by others.*
 - Should the unidentified hydrocarbon mass be included? *While the unidentified should be included in the ratio, analytical efforts should be made to reduce the unidentified fraction.*
 - Is VOC above a cut-off limit? *Researchers often exclude VOC and NO_x data when VOC concentrations are below a cut-off (say 100 ppbC) to avoid cases close to the detection limit.*

VOC typically is defined as C2-C10 nonmethane hydrocarbons measured by gas chromatography-flame ionization detection (GC-FID) including biogenics, unidentified mass and excluding carbonyl compounds (NRC, 1991). Analysts should define their ratios.

Analyses using VOC/NO_x Ratios (2 of 3)

The analyst needs to consider the following (continued):

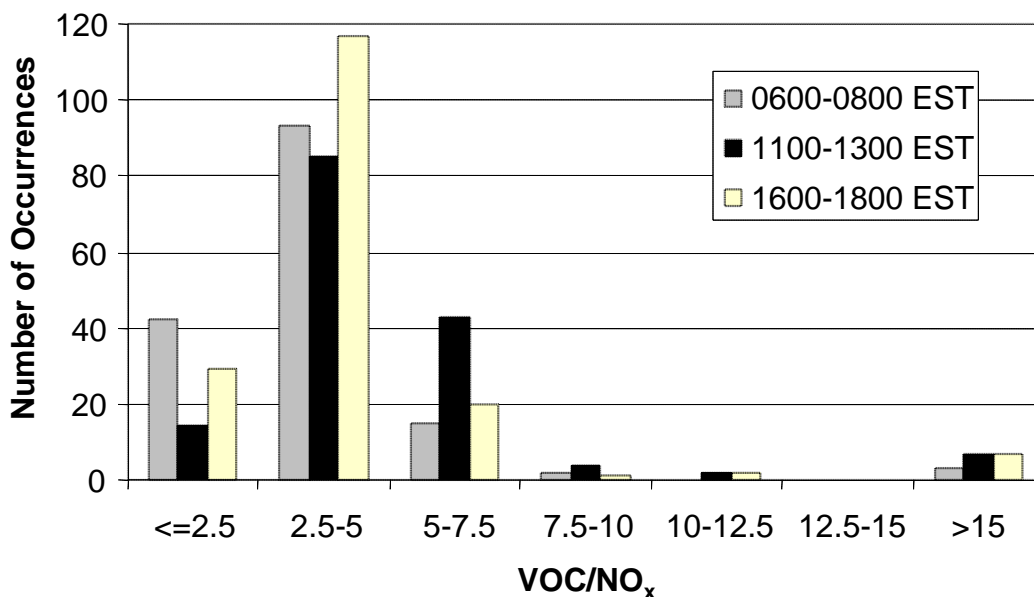
- What comprises NO_x in VOC:NO_x?
 - Adjusted NO_x? NO_y? Only NO_x or NO_y above a cut-off limit? *Researchers typically use the available data (usually NO_x) and often exclude VOC and NO_x data when NO_x concentrations are below a cut-off (say 5 ppb) to avoid cases close to the detection limit.*
 - Time standard for the ratio - standard or local? *Local time aligns the analysis with people's activities, but standard time is often used.*
 - Time of day of the ratio? *Morning (6 a.m.-9 a.m.) is often used, but ratios for midday and afternoon are also useful.*
 - Subtract out NO_x or VOC background concentrations? *This can be done, in order to minimize the influence of background concentrations.*

Analyses using VOC/NO_x Ratios (3 of 3)

The analyst needs to consider the following (concluded):

- When pollutant transport is a significant or dominant factor in high ambient concentrations at a site, precursor concentrations at upwind locations along the transport path need to be determined.
- Identify ozone contributions from local precursor emissions, transported ozone formed in upwind locations, in-situ ozone production from transported upwind precursors.
- Analyses include frequency distributions of ratios by site and by time of day; scatter plots of VOC and NO_x to assess relationships; spatial and temporal variations in ratios; and ratios as a function of time of day or along a trajectory.

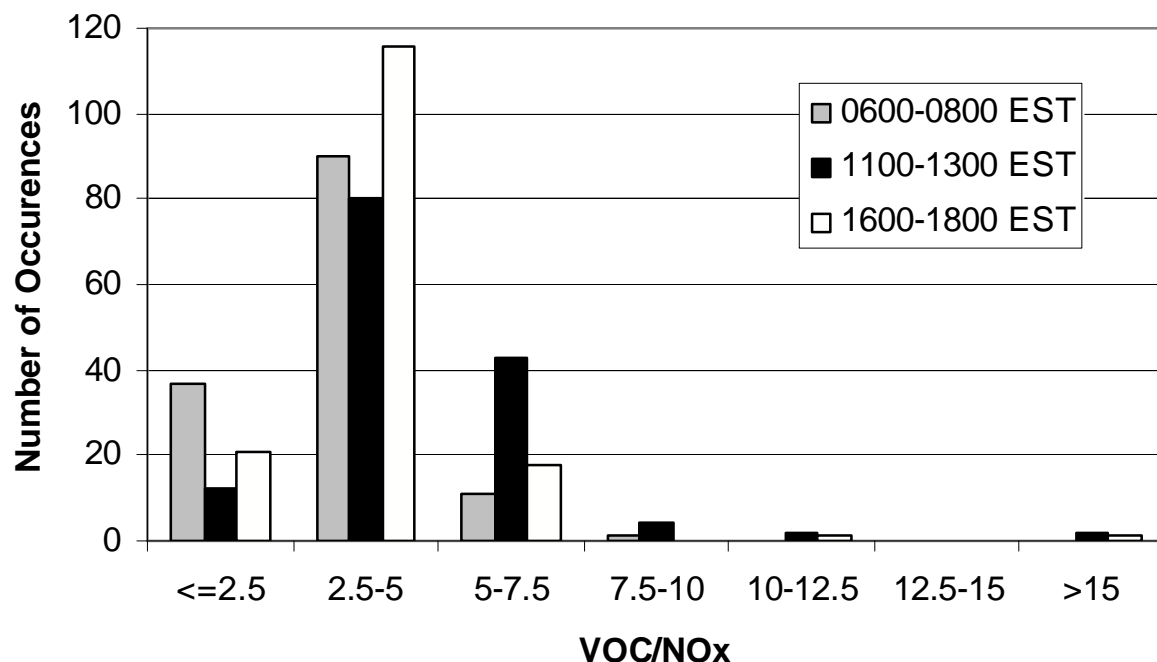
Distribution of VOC/NO_x Ratios (1 of 2)



Histogram of the number of hours with VOC/NO_x ratios in selected ranges by time of day. Data are from an urban PAMS site during June-August 1998. Distribution determined using Excel Tools/Data Analysis/Histogram.

- In this example of the distribution of VOC/NO_x ratios at an urban PAMS site, most of the morning VOC/NO_x ratios indicate VOC-limitations (< 5 ppbC/ppb). However, note that several morning ratios fall within the transitional range (about 5 to 15 ppbC/ppb) and a few ratios show NO_x limitations (> 15 ppbC/ppb). The distribution among the ratios by time of day is relatively similar which is consistent with the site's proximity to fresh emissions all day (note, however, that midday and afternoon ratios are judged by different criteria).
- This example is meant to illustrate a way to investigate data, not as a general guide on the distribution of VOC/NO_x ratios.

Distribution of VOC/NO_x Ratios (2 of 2)

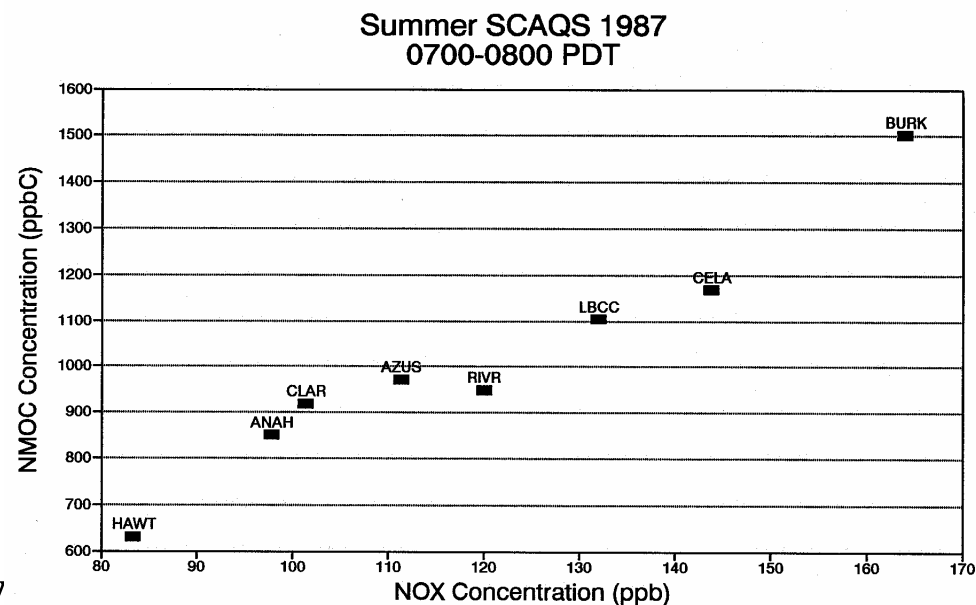


Histogram of the number of hours with VOC/NO_x ratios in selected ranges by time of day. Data are from an urban PAMS site during June-August 1998. Distribution determined using Excel Tools/Data Analysis/Histogram. Data were screened to include only [NO_x] ≥ 5 ppb and [VOC] ≥ 100 ppbC.

- This example uses the same data set as the previous figure with the exception that data screens were employed. Ratios were only counted that met the following criteria: NO_x ≥ 5 ppb and VOC ≥ 100 ppbC. This allows the analyst to screen out data that may be close to the instrument detection limits.
- The distribution among the ratios by time of day is very similar to the previous plot with the exception that fewer ratios above 7.5 are noted once screening criteria are applied.

VOC and NO_x Scatter plots

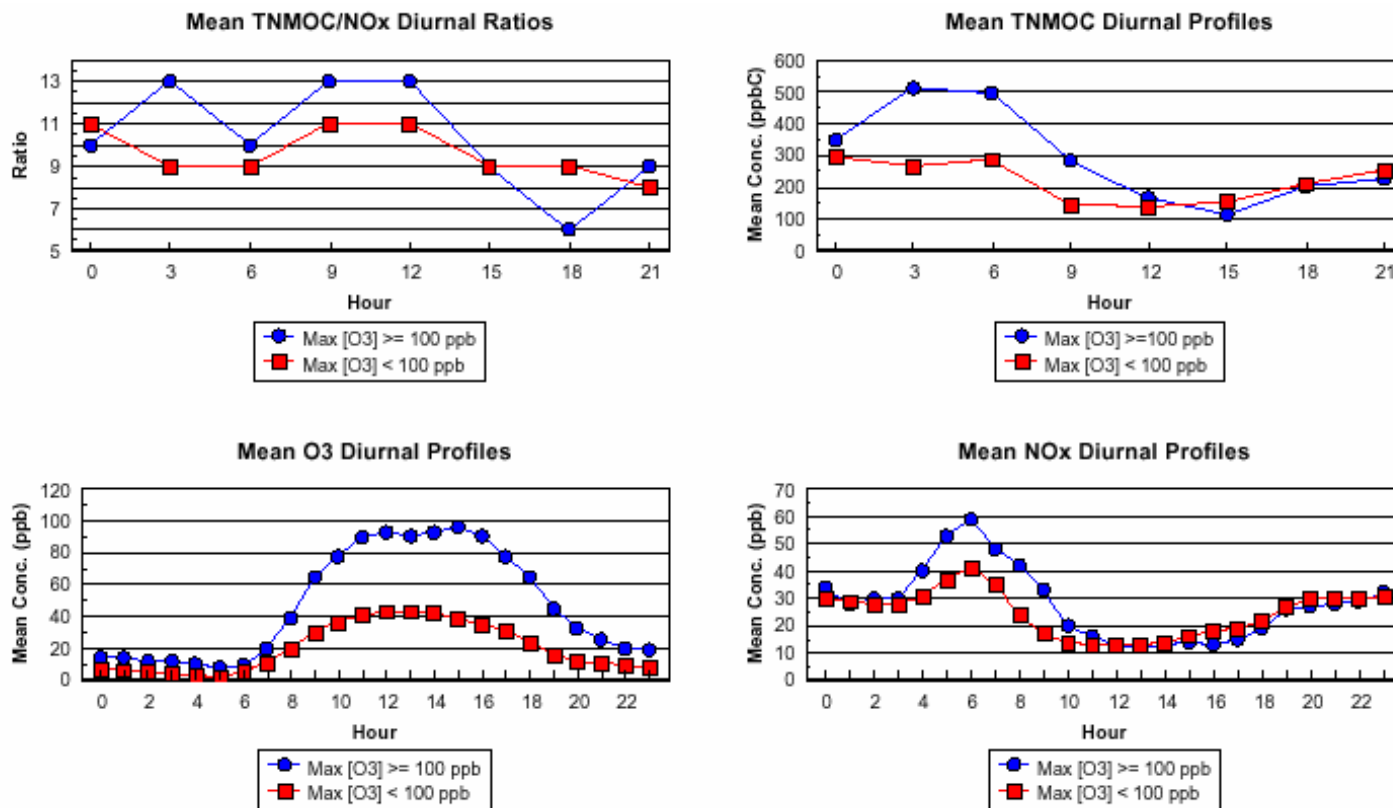
- Scatter plots of individual sample VOC and NO_x concentrations, or site averages, can be inspected. A good correlation between VOC and NO_x implies a common emission source.
- When the average ratios by site were considered in this example, the VOC and NO_x correlate very well ($r^2 = 0.94$).



SCAQS summer morning (0700-0900 PDT) NMOC and NO_x concentrations (Lurmann and Main, 1992) averaged by site where NMOC = NMHC + C1-C7 carbonyl compounds.

Spatial and Temporal Variations in VOC/NO_x

Baton Rouge Capitol Site, June-August 1996

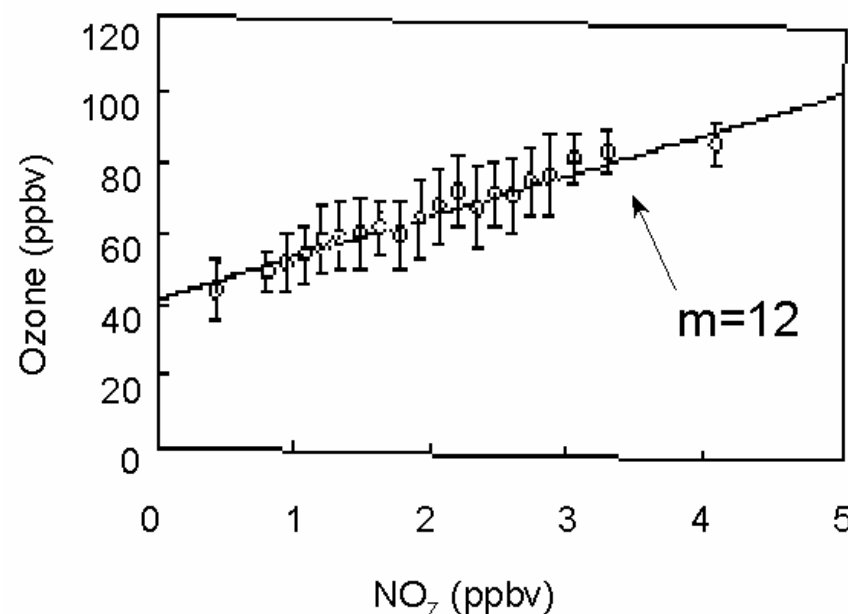


- Diurnal analyses of TNMOC, NO_x, TNMOC/NO_x ratios, and ozone for the urban Baton Rouge site in 1998. Diurnal profiles are compared for days in which the maximum 1-hr ozone concentration was ≥ 100 ppb with days of maximum 1-hr ozone < 100 ppb.
- Elevated mean NO_x and TNMOC concentrations were observed on ozone episode days. An analysis of meteorology (e.g., mixing heights, surface winds) would enhance this analysis (Sather and Kemp, 1998).

Relationships of Ozone, NO_y , and NO_z

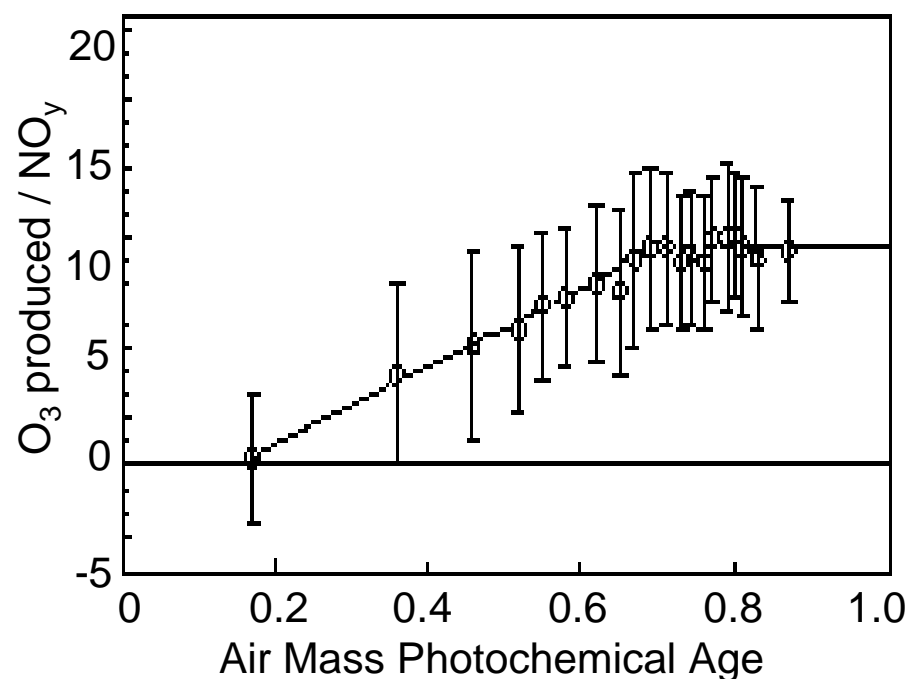
- **Ozone with NO_y :** correlates well in a NO_x -limited regime and correlates poorly in a VOC-limited regime.
- **Ozone with NO_z :** if the slope of the relationship is $>$ about 10, the air mass is likely NO_x -limited. If the slope of the relationship is $<$ about 8, the air mass is likely VOC-limited.

Relationship of NO_x , NO_y , and NO_z to Ozone Formation



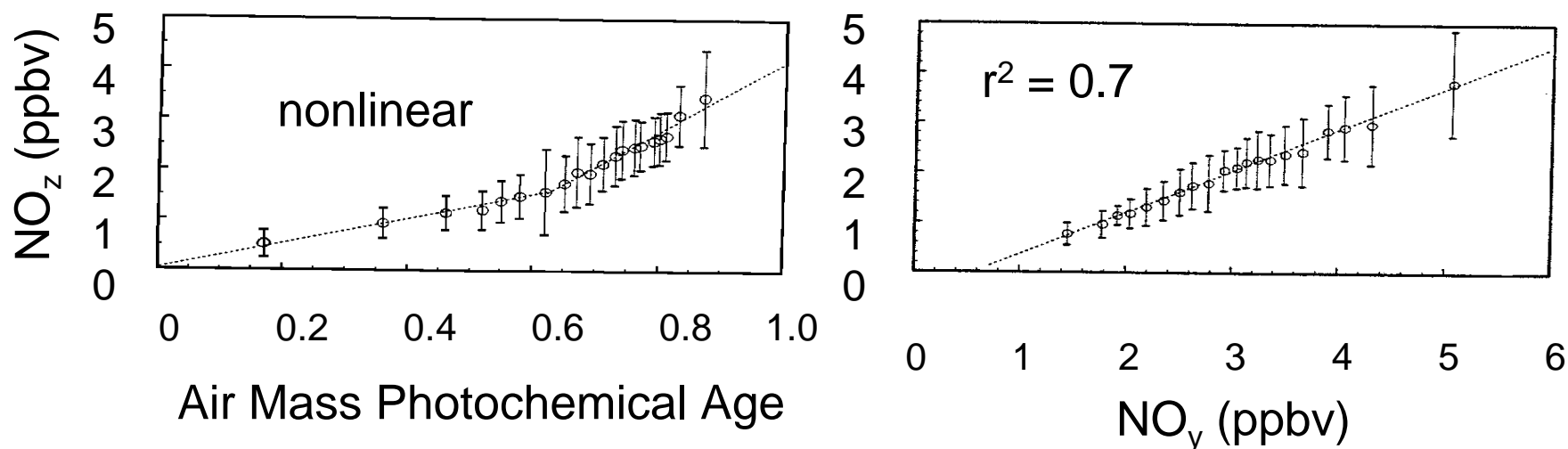
The slope of $[\text{O}_3]$ versus $[\text{NO}_z]$ yields the ozone production efficiency. There, the slope = 12; therefore, 12 molecules of ozone are formed for each molecule of NO_x consumed (Olszyna et al., 1994). Data are binned and centered in the respective interval. The bars give the standard deviation.

Relationship of NO_x , NO_y , and NO_z to Ozone Formation (1 of 2)



Ozone production efficiency may be examined with plots of ozone and photochemical age. Net ozone production continues until about 70% of the NO_x emitted has been converted into NO_2 . In other words, at a photochemical age ≥ 0.6 to 0.7, the smog-forming potential of the atmosphere is exhausted (Olszyna et al., 1994; Giles County, Tennessee data). Data are binned and centered in the respective interval. The bars give the standard deviation.

Relationship of NO_x , NO_y , and NO_z to Ozone Formation (2 of 2)



Ozone production efficiency is a complex issue. Note that $\text{NO}_z = \text{NO}_y$ * Photochemical Age. The linearity of the second plot shows that NO_z depends only on NO_y rather than Photochemical Age, or on both factors (Olszyna et al., 1994; Giles County, Tennessee data).

Indicator Methods (1 of 2)

Indicator (Afternoon)	Threshold for NO _x -Limitation	Reference
NO _y	< 10 to 25 ppb	Milford et al., 1994
NO _z	< 5 to 20 ppb	Milford et al., 1994
O ₃ /NO _y	>5 to 10 >3 to 6*	Sillman, 1995; Jacob et al., 1995 Sillman et al., 1997
O ₃ /NO _z	> 6 to 11 > 6 to 9	Sillman, 1995; Jacob et al., 1995 Sillman et al., 1997
(O ₃ - 40 ppb)/NO _y	> 4	Sillman, 1995; Jacob et al., 1995
HCHO/NO _y	> 0.2 to 0.4	Sillman, 1995; Jacob et al., 1995
H ₂ O ₂ /HNO ₃	> 0.3 to 0.5 > 0.1 to 0.3	Sillman, 1995; Jacob et al., 1995 Sillman et al., 1997
H ₂ O ₂ /NO _y	>0.2 to 0.4 > 0.1 to 0.2	Sillman, 1995; Jacob et al., 1995 Sillman et al., 1997
H ₂ O ₂ /NO _z	>0.2 >0.1 to 0.3	Sillman, 1995; Jacob et al., 1995 Sillman et al., 1997
O ₃ /HNO ₃	> 7 to 11	Sillman et al., 1997
Morning NMOC/NO _x	> 10 to 15	National Research Council (1991)
Afternoon NMOC/NO _x	> 15 to 20	National Research Council (1991)

* 50th percentile of simulations

Indicator Methods (2 of 2)

- Edgerton and Hartsell (1996) reported on a source classification approach to identify the probable dominant contributor(s) of NO_y . The table at top right lists their criteria (note that both ratios must meet the criteria). For their analysis, a dominant contributor was defined as a source that could provide at least 75 % of observed NO_y based on tabulated tracer: NO_y ratios.
- Results of their analysis are shown in the second table for a rural Pennsylvania site. They concluded that urban emissions contributed greater than 75% of the observed NO_y for 6 episode days and never contributed less than 25%.

Ratio	Urban	Mixed	Major Pt. Source
CO^*/NO_y	> 10:1	>5:1	<5:1
SO_2/NO_y	<0.5:1	>0.5:1	>1.5:1

where CO^* =observed CO less the northern hemispheric background of 80 ppb (Parrish, 1980)

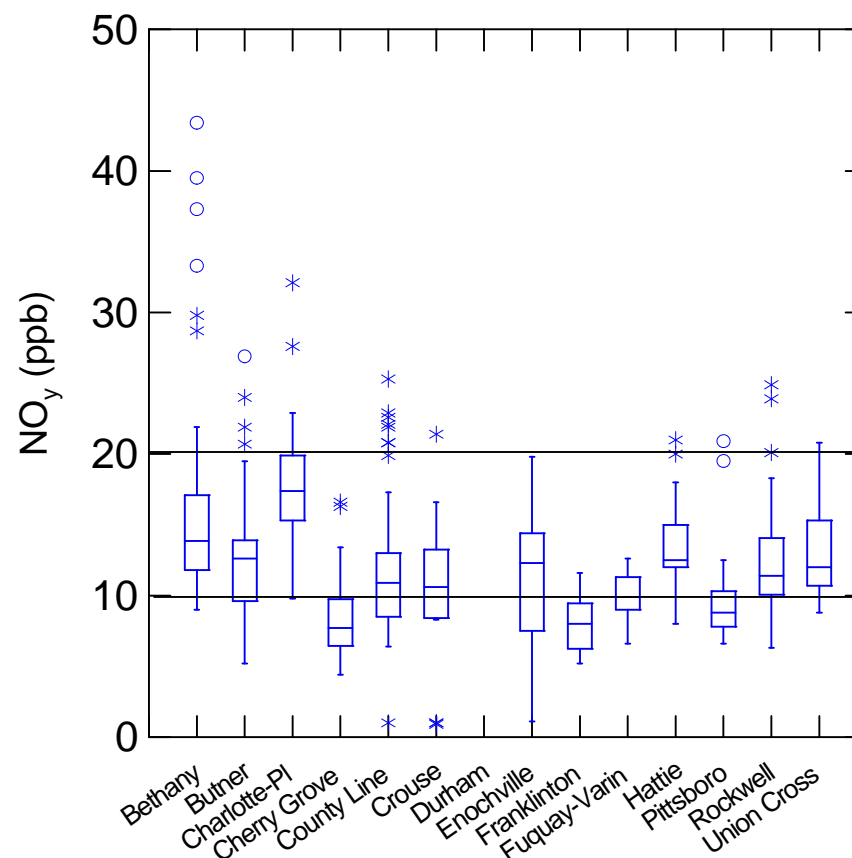
Summary of 1995 Ozone Episodes at Arendtsville, PA.

DATE	O3	NO_y	CO^*	SO_2	CO^*/NO_y	SO_2/NO_y	Episode Class
6/17/95	80.88	9.70	143	7.31	14.79	0.75	M
6/18/95	80.09	7.17	131	5.02	18.21	0.70	M
6/19/95	105.41	14.33	167	17.46	11.64	1.22	M
6/20/95	80.65	8.96	172	5.64	19.19	0.63	M
6/21/95	85.78	24.79	209	16.15	8.42	0.65	M
7/12/95	80.75	7.03	157	3.02	22.31	0.43	U
7/13/95	92.54	9.58	148	3.98	15.41	0.42	U
7/14/95	90.31	8.82	119	3.92	13.44	0.44	U
7/15/95	90.01	8.98	95	5.52	10.62	0.62	M
7/16/95	81.86	8.30	89	2.45	10.73	0.30	U
7/22/95	84.80	11.64	178	5.29	15.33	0.45	U
7/31/95	91.23	8.70	91	5.81	10.41	0.67	M
8/1/95	88.73	7.77	123	4.77	15.81	0.61	M
8/15/95	86.83	11.90	122	5.14	10.25	0.43	U
8/16/95	103.45	14.64	150	11.64	10.25	0.80	M
8/17/95	87.05	8.34	70	5.73	8.39	0.69	M
8/21/95	87.98	8.04	120	7.30	14.97	0.91	M
8/24/95	91.14	10.00	126	13.56	12.63	1.36	M
8/26/95	85.35	9.87	124	6.74	12.55	0.68	M
8/31/95	86.21	8.35	83	7.74	9.98	0.93	M
9/8/95	86.54	14.33	126	21.55	8.79	1.50	M

Where M=mixed, U=urban; ozone concentrations are 8-hr; all concentrations are in ppb. From Edgerton and Hartsell (1996).

Example Indicator Methods

- This example shows a box plot of NO_y concentrations between 1100 and 1800 EST at several sites in North Carolina. Horizontal lines are drawn to indicate afternoon NO_y threshold concentrations of 10 to 20 ppb.
- Most of the afternoon NO_y concentrations were in the transitional regime with a few rural downwind sites (Cherry Grove, Franklinton, and Pittsboro) showing some NO_x -limitations.
- Other analyses applied to these data included inspection of morning VOC/ NO_y ratios, NO_y to ozone correlations, and observational-based modeling to arrive at consensus among results.



MacDonald et al., 1998

Observational-based Modeling

Objectives of observational-based modeling include:

- Identifying spatial and temporal characteristics of VOC-limited and NO_x-limited conditions.
- Corroborating emission-based models prospectively.
- Assisting monitoring network design.

Topics covered in this section include:

- Review of the smog production algorithm (SPA).
- What is “Measurement-based Analysis of Preferences in Planned Emission Reductions” (MAPPER)?
- Example applications.

Smog Production Algorithms (1 of 2)

- The smog production algorithm was developed by Johnson (1984); derived empirically from smog chamber data.
- The purpose of the SPA is to determine ozone formation sensitivity to changes in NO_x concentrations.
- Ozone, NO , and NO_x (or NO_y) concentrations are used to compute Smog Produced (SP) and the Extent of Reaction (E):

$$\begin{aligned}\mathbf{SP(t)} &= \mathbf{O_3(t) - O_3(0) + NO(0) - NO(t)} \\ \text{smog} &= \text{ozone produced} + \text{oxidized NO}\end{aligned}$$

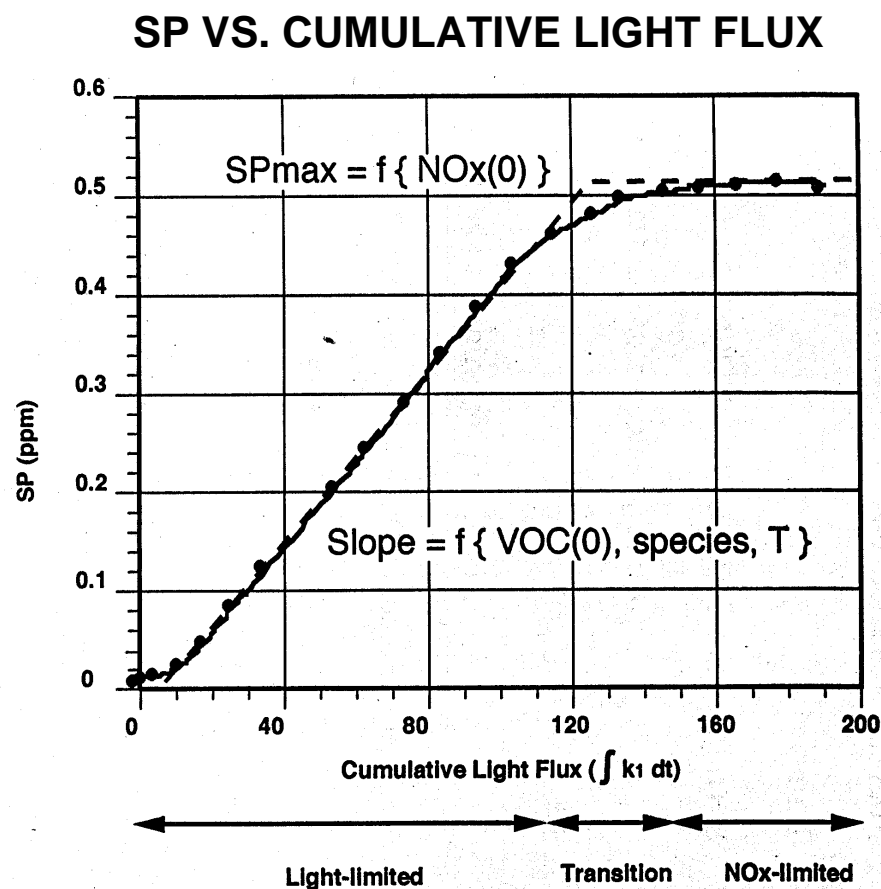
$$\begin{aligned}\mathbf{SP_{max}} &= \beta(\text{NO}_x(i)) \\ \text{Maximum smog produced} &\propto \text{NO}_x \text{ inputs}\end{aligned}$$

$$\mathbf{E} = \text{SP}(t) / \text{SP}_{\text{max}}$$

$$t = \text{time, where 0 denotes initial conditions}$$

Smog Production Algorithms (2 of 2)

- Smog Production (SP) responds linearly to cumulative light flux (see figure); consequently accounting for the NO-ozone co-dependence.
- SPA is consistent with fundamental atmospheric chemistry processes; changes in SP over time is an indicator of the rate of NO oxidation by peroxy radicals.
- Modifications to SPA have been made to adapt the equation to real atmospheric conditions in the United States (e.g., Blanchard et al., 1993a, 1993b, 1994a, 1994b, 1999).



Example smog chamber data showing increase in smog produced (SP) with cumulative light flux (Johnson and Quigley, 1989). SP eventually reaches a maximum (SP_{max}) and the air parcel becomes NO_x -limited.

What is MAPPER?

- MAPPER is Windows-based software that estimates the "relative" degree of NO_x - and VOC-limiting conditions, based on hourly ozone and NO_x (or NO_y) measurements, by applying the modified SPA.
- The original motivation behind MAPPER was to develop an observational technique that was more robust than simply using VOC/ NO_x ratios.
- MAPPER was developed by ENVAIR, originally funded by EPA, and subsequently by API and others.
- MAPPER is available from <http://capita.wustl.edu/EnhancedOzone/> under Resources/Reports:Tools:Ozone: Mapper

MAPPER Data Requirements

Data excerpt

Aurora (IL)	ES01	88.48870	41.73300	910626	0	20.0	0.3	31.5
Aurora (IL)	ES01	88.48870	41.73300	910626	1	17.0	0.1	31.1
Aurora (IL)	ES01	88.48870	41.73300	910626	2	12.0	0.6	30.3
Aurora (IL)	ES01	88.48870	41.73300	910626	3	12.0	0.8	27.8
Aurora (IL)	ES01	88.48870	41.73300	910626	4	16.0	1.6	27.9
Aurora (IL)	ES01	88.48870	41.73300	910626	5	19.0	7.1	30.6
Aurora (IL)	ES01	88.48870	41.73300	910626	6	18.0	2.1	24.1
Aurora (IL)	ES01	88.48870	41.73300	910626	7	30.0	2.4	21.3
Site name	Site code	Long.	Lat	yymmdd	Hr	O ₃	NO _x	NO _y

Data requirements

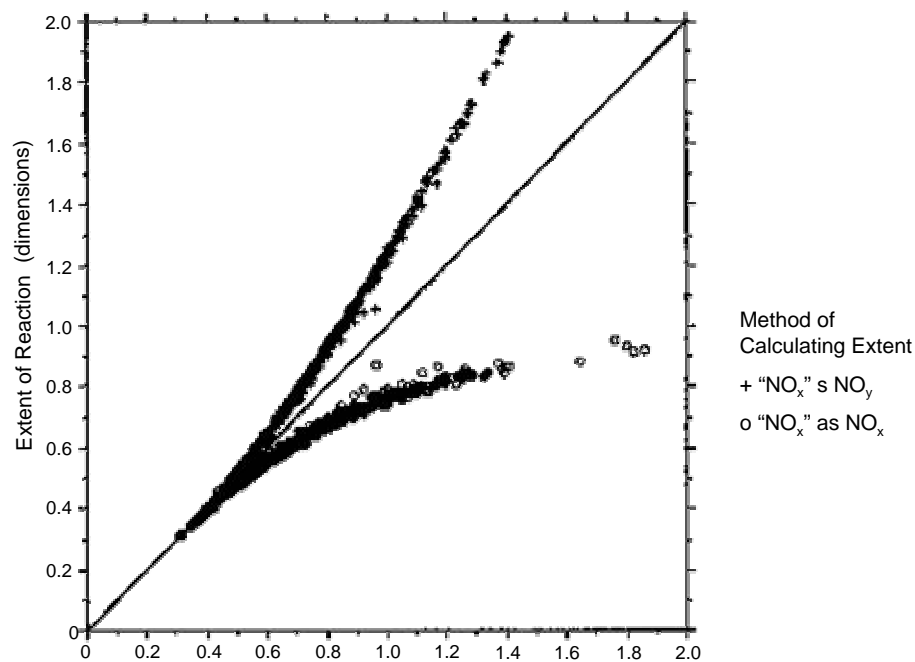
- MAPPER will handle up to 3000 site-days of data.
- No blank or incomplete lines of data (missing data = -9.0 or -99.9) are allowed.
- Data should be ordered in increasing hours.
- See the user's guide for additional information (Blanchard and Roth, 1995).

Extent of Reaction

- When E approaches 1, smog production ceases because virtually all of the NO_x has reacted. Thus, $E > 0.9$ is strongly indicative of a NO_x -sensitive air mass.
- $E < 0.6$ is strongly indicative of a VOC-sensitive (VOC-limited) air mass.
- $0.6 < E < 0.9$ suggests a transition to a NO_x -sensitive air mass.

Issues of Bounding NO_x , NO_y

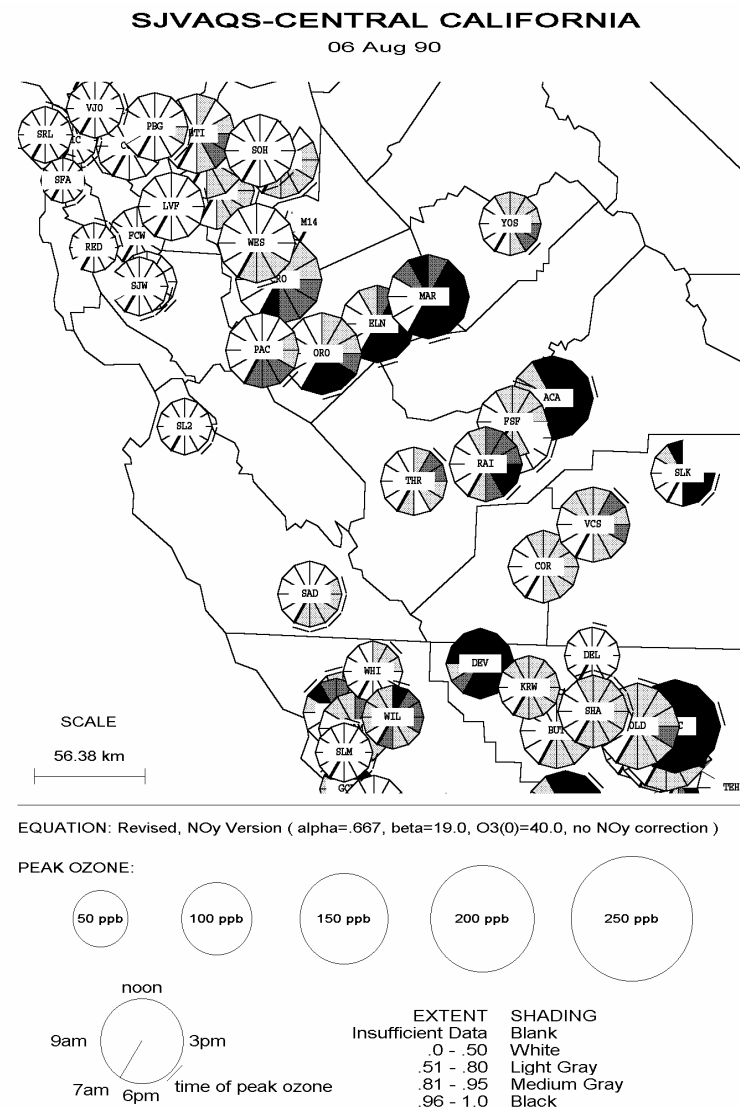
- The analyst may have available only traditional NO_x measurements (i.e., $\text{NO} + \text{NO}_2$ + poorly defined amounts of other nitrogen species). These NO_x measurements represent neither true NO_x nor true NO_y . When only NO_x measurements are available, it is possible to bound the extent of reaction by using these data to compute E using both the NO_x and NO_y versions of the algorithm.
- True extent lies somewhere between the bounds shown in the figure. NO_x measurements overestimate true $\text{NO} + \text{NO}_2$ but underestimate true NO_y .



Blanchard et al., 1999;
Blanchard and Roth, 1995.

Spatial and Temporal Extent (1 of 3)

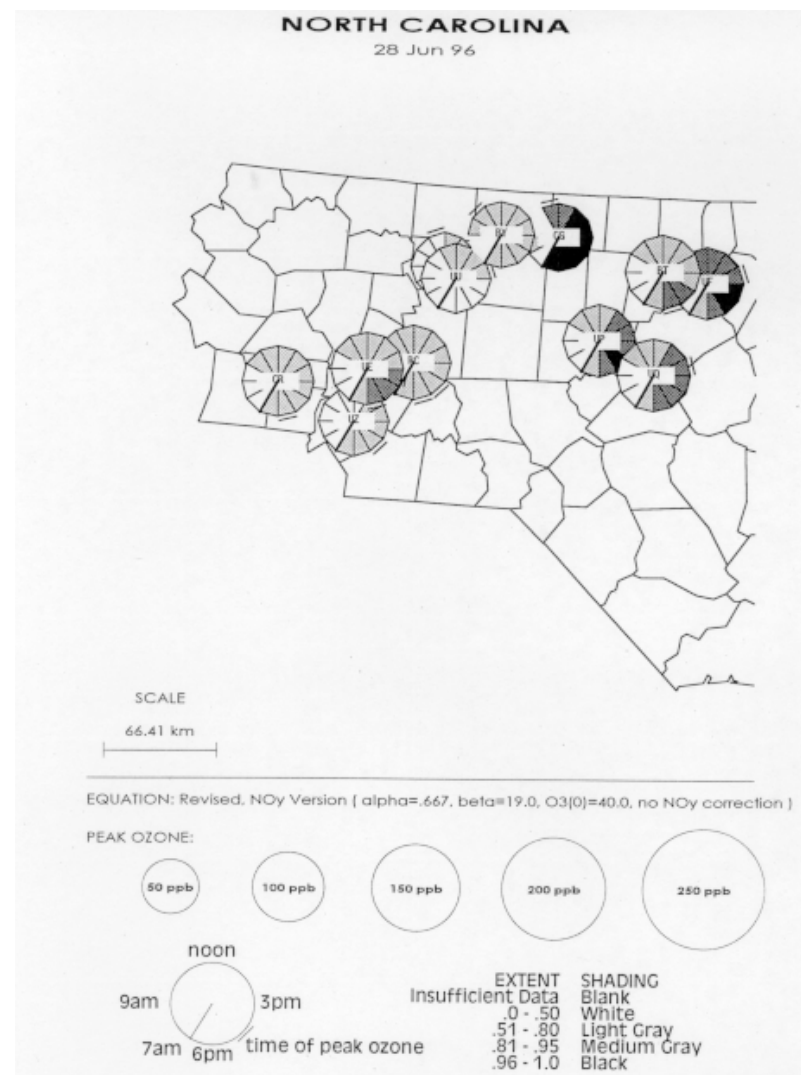
- This example shows MAPPER output from the 1990 San Joaquin Valley Air Quality Study for August 6, 1990.
- Extent of reaction results for each site are given for daylight hours (7 a.m. to 6 p.m. ST) using shading.
- The size of the circle containing the extent information is scaled to peak the ozone concentration.
- The more downwind sites exhibited higher ozone concentrations and higher extent of reaction.



Blanchard, 1997

Spatial and Temporal Extent (2 of 3)

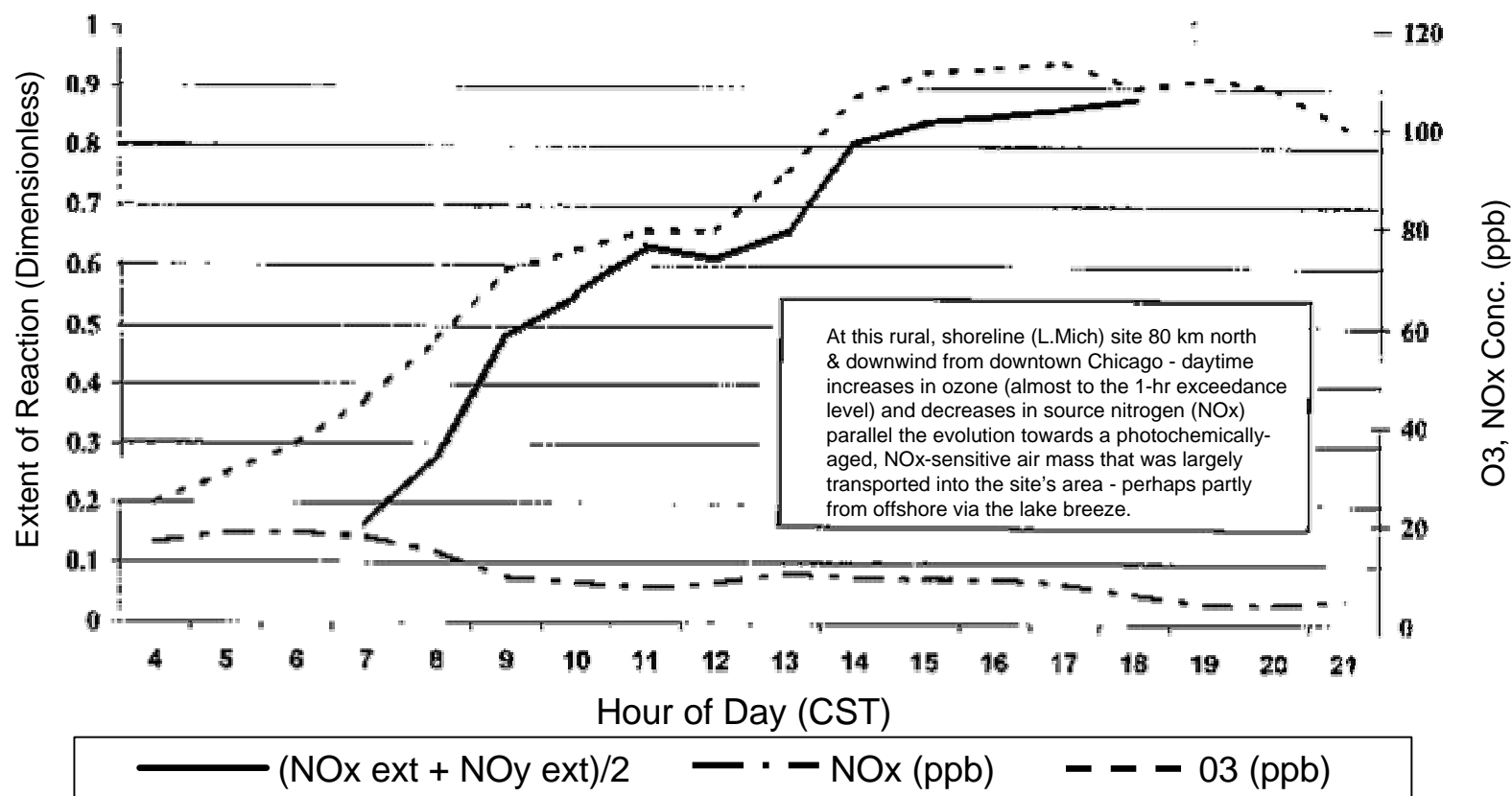
- Does extent of reaction approach one (i.e., darker in the plot) during hours when ozone concentrations are at or near peak values at a site?
- For how many hours does the extent of reaction approach one?
- Does extent approach one at the sites having the highest ozone concentrations?
- This example shows the extent of reaction was higher at a given site during the time of peak ozone, and the urban sites were more VOC-limited (denoted as white to light gray) than the downwind sites consistent with expectations.



MacDonald et al., 1998

Spatial and Temporal Extent (3 of 3)

Average Hourly Extent of Reaction Calculations



Assume 40 ppb O₃ tropospheric background.

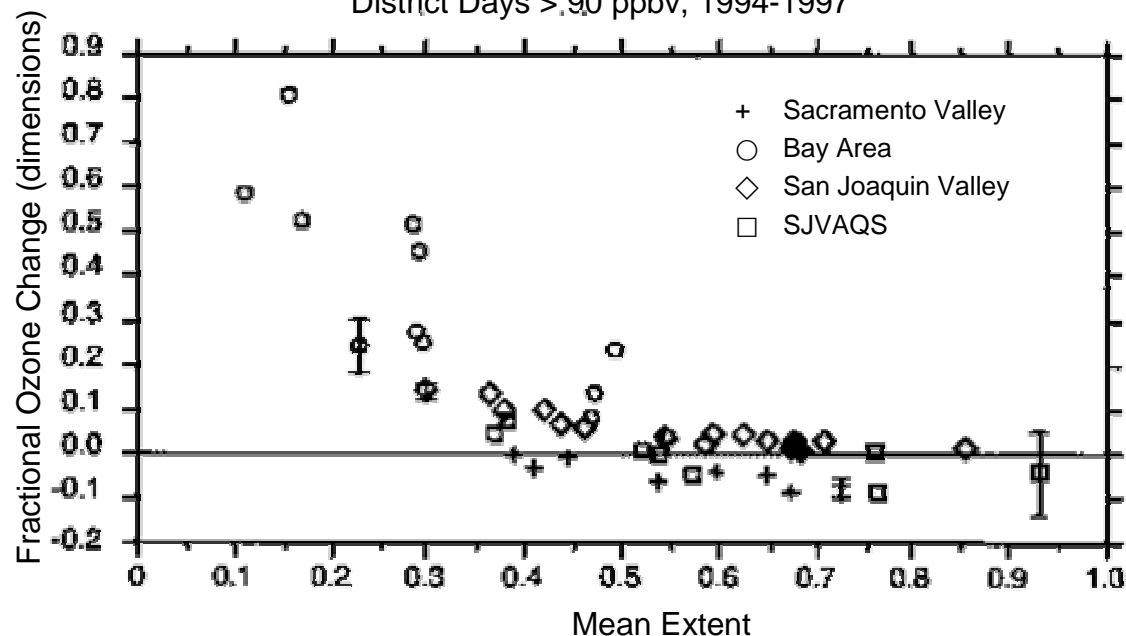
Camp Logan, IL (near Lake Michigan), June 17, 1995

Adamski, 2000

Assessing Day of Week Differences (1 of 2)

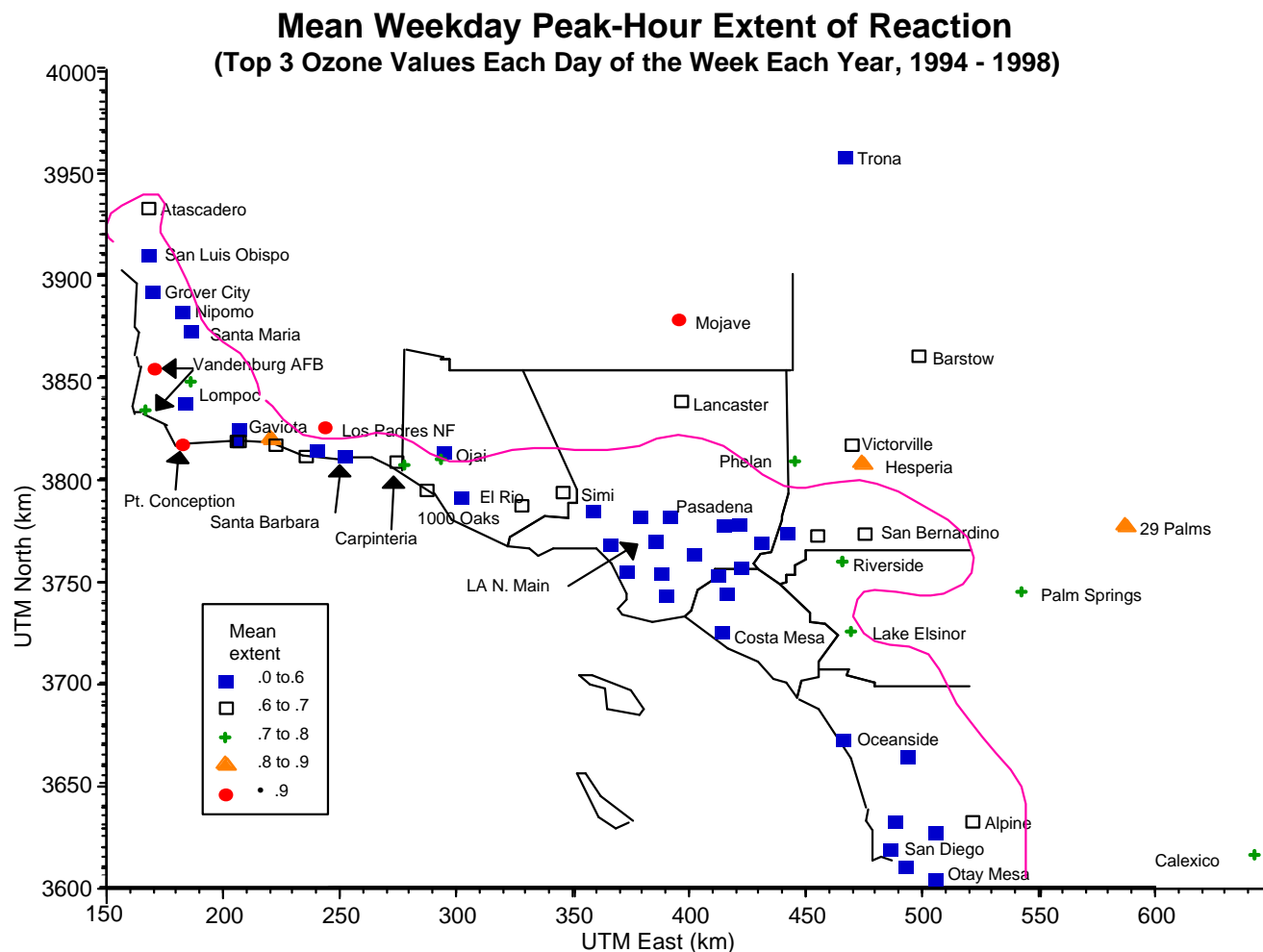
- In this example, an exploration of the variation in a site's ozone response to lowered weekend precursor levels is examined. To normalize for the variation among sites in the mean ozone and NO_x concentrations, the difference between mean weekend and weekday peak ozone was divided by the mean weekday values. This yields a dimensionless quantity that reflects the fractional change in ozone from weekday to weekend.
- Sites having low mean extent of reaction showed increases in peak ozone levels from weekday to weekend. All San Francisco Bay Area sites are in this group.

In Northern California, Weekend - Weekday Peak
Ozone Differences are Related to
the Extent of Reaction
Mean Weekend Peak Ozone Minus mean Weekday Peak Ozone
versus
Mean Extent of Reaction at the Time of the Peak Ozone
District Days > 90 ppbv, 1994-1997



Blanchard, 2000.

Assessing Day of Week Differences (2 of 2)



Blanchard, 2000

This example shows mean weekday peak-hour (for ozone) extent of reaction in Southern California. The example is based on the top three ozone values each day of the week for each year during 1994-1998. Note that coastal and Los Angeles basin sites (as denoted by the curved line) show mostly VOC limitations. This plot can then be compared to a similar plot for weekends.

Other Methods

An observational-based model (OBM) was developed by Cardelino and Chameides (1995):

- The OBM requires hourly speciated hydrocarbon, NO, CO, and ozone concentrations as well as temperature, relative humidity, and mixing height.
- When concentration fields from the urban airshed model were input into the OBM, the two models predicted similar sensitivities to VOC and NO_x.

Analysis Along a Transport Path (1 of 2)

Time of Day	Location	O ₃ (ppb)	NO _x (ppb)	NMOC/ NO _x
Early morning	Aloft along boundary	60-86	3	14-28
Early morning	Chicago	18	210	4
	Gary	34	32	7
	Milwaukee	35	46	6
Mid morning	Zion	85	16	8
	Mid-lake Boat	82	11	9
Afternoon	South-lake Boat	129	6	16 *
	Aloft over South-lake Boat	125	9	6
	Aloft over North-lake Boat	106	11	6
	North-lake Boat	148	20	7
	Sheboygan	134	14	12
	Aloft over NEROE intersection	121	6	13 *
	Aloft over Collins	99	2	33
Late afternoon	North-lake Boat	119	5	9 *
	Aloft over North-lake Boat	76	6	14
	Sheboygan	111	4	17 *

NMOC = NMHC + formaldehyde and acetaldehyde

Samples were selected along an estimated time/distance path similar to an estimated trajectory for a polluted air parcel which might have arrived at the location of the maximum ozone concentration. The extent of reaction was about one (indicating NO_x limitations) for those samples with * in the NMOC/NO_x column (Roberts et al., 1995b).

Analysis Along a Transport Path (2 of 2)

Date (1991)	Time (CDT)	Location	O ₃ (ppb)	NO _x (ppb)	NMOC/ NO _x
June 26	1300-1500	South-lake Boat	129	6	16 *
June 26	1300-1500	North-lake Boat	148	20	7
June 26	1300-1500	Sheboygan	134	14	12
June 28	1455-1458	Aloft over Mid-lake Boat	127	5	8
July 17	1802-1803	Aloft over Tulip City	151	8	7
July 18	1309-1311	Aloft over NEPTS intersection	135	18	7
July 18	1300-1500	Mid-lake Boat	154	12	9
July 18	1427-1431	Aloft over Mid-lake Boat	136	5	12 *
July 18	1700-1900	Borculo	164	9	17 *
July 18	1804-1805	Aloft over Tulip City	154	8	9 *

NMOC = NMHC + formaldehyde and acetaldehyde

NMOC/NO_x, and ozone and NO_x concentrations, for all LMOS NMOC samples with ozone concentrations greater than 125 ppb. The mean NMOC/NO_x ratio is 10 and the median ratio is 9. The extent of reaction was about one (indicating NO_x limitations) for those samples with * in the NMOC/NO_x column (Roberts et al., 1995b).

Method and Tool Availability

- **Data Sources:**
 - AIRS Data via public web at <http://www.epa.gov/airsdata>
 - AIRS Air Quality System (AQS) via registered users register with EPA/NCC (703-487-4630)
 - Meteorological parameters from National Weather Service (NWS) <http://www.nws.noaa.gov>
 - Meteorological parameters from PAMS/AIRS AQS register with EPA/NCC (703-487-4630)
- **Data Display and Investigation:**
 - Statistical software and related tools (e.g., AMDAS from <http://www.environ.org/amdas>).
 - Spreadsheets and graphical packages
- **Observational Driven Methods:**
 - MAPPER is available from <http://capita.wustl.edu/EnhancedOzone/> under Resources/Reports:Tools:Ozone:Mapper

Summary

In this section, the relationships among NO_x , NO_y , VOC, and ozone are discussed including VOC/ NO_x ratios and the extent of photochemical aging. By understanding these relationships, the analyst can begin to assess control strategies for reducing ozone concentrations.

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